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THE RELATIONSHIP OF THE WATER QUALITY OF THE ST. CROIX RIVER TO PULP MILL EFFLUENT DISCHARGE

IWD-AR-WQB-84-59

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

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ENVIRONMENT CANADA

Geoffery Howell

Water Quality Branch
Atlantic Region
Moncton, New Brunswick

March 31, 1984

This report is available in French upon request

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LETTER OF TRANSMITTAL

Chairman, Canadian Section
IJC Advisory Board
St. Croix River

Gentlemen:

Re: Report on Response of the St. Croix River to Pulp Mill Effluent

This report describes the response of the major ion concentrations of the St. Croix River during a twelve day period of variable pulp mill effluent loading. In addition, a nomogram is presented which can predict dissolved oxygen saturation from specific conductance and water temperature.

Observations and comments on this report would be welcome.

Yours Sincerely,

D. H. Cullen, Chief
Water Quality Branch

ABSTRACT

Water samples were collected on twelve hour intervals from the St. Croix River at Milltown during the period of September 1, 1983 to September 13, 1983. This corresponded to a period of temporary shut-down and subsequent reduced effluent discharge from the Georgia-Pacific Corporation pulp mill located at Woodland, Me. Flow weighted effluent BOD concentrations at Woodland were found to be related to Milltown concentrations of those major ions significantly affected by effluent loading. Using these relationships, it appeared that there was a 24 hour lag in response at Milltown to reduced effluent loading 14 km upstream at Woodland.

A nomogram is presented which predicts the dissolved oxygen saturation at Milltown from specific conductance and water temperature. The predictability of this nomogram is discussed using selected grab sample and automatic monitor data sets. Although predictability is poor below 65% saturation, it is felt that this nomogram is still useful in an "early-warning" capacity.

RÉSUMÉ

Des échantillons d'eau furent prélevés de la Rivière Ste-Croix à Milltown, à des intervalles de douze heures, durant la période du 1 septembre 1983 au 13 septembre 1983. Cette période correspond à la fermeture temporaire et au débit d'effluent subséquent réduit du moulin à pulpe de la Georgia-Pacific Corporation située à Woodland, Me. A Milltown, les concentrations de certains ions principaux dans la rivière sont affectées significativement par le débit de l'effluent. Il existe une relation entre celles-ci et les concentrations en DBO de l'effluent corrigées selon le débit, à Woodland. En considérant ces relations, il semble exister un délai de 24 heures pour percevoir à Milltown l'effet de la réduction du débit de l'effluent à Woodland, 14 km en amont.

Un nomogramme est présenté, prédisant la saturation en oxygène dissout à Milltown, à partir de la conductivité spécifique et la température de l'eau. L'habilité de prédire de ce nomogramme est discutée en utilisant certains échantillons sélectionnés et des groupes de valeurs provenant du moniteur automatique. Bien que l'habilité de prédire est faible en dessous de 65% de saturation, il est perçu malgré tout que ce nomogramme peut être utile pour ses possibilités d'avertissement rapide.

INTRODUCTION

The St. Croix River forms the international boundary between Canada and the United States and has a length of approximately 124 kilometers. Although the upper 110 km of the river are considered to be pristine, it is the lower 14 km section between Woodland, Me. and Milltown, N.B. which is of water quality concern. The problems in the lower reaches of the St. Croix River result from a major industrial discharge at Woodland, Maine and to a lesser extent from municipal discharge and combined sewer overflows in Woodland and Baileyville, Maine. The Georgia-Pacific Corporation operates a Kraft Pulp Mill at Woodland, Maine, which produces fully bleached Kraft pulp, and discharges Kraft Mill effluent through a secondary waste treatment facility into the St. Croix River. Since 1977, modifications to the plant and strict control on effluent and river discharge have greatly improved the water quality of the lower reach of the river (Howell and Lockerbie, 1983) such that it is now capable of supporting an anadramous run of Atlantic Salmon (Salmo salar).

Although the overall water quality conditions allow fish passage, the river experiences infrequent episodes of high effluent loading during periods of low river discharge. These events result in significant increases in total dissolved salts and BOD loads, followed by subsequent drastic reductions in dissolved oxygen saturation.

From September 4, 1983 to September 18, 1983, the Georgia-Pacific

Kraft Pulp Mill was shut down for routine maintenance which provided an opportunity to investigate the response of the St. Croix River to varying effluent loads. Therefore, samples were collected at regular intervals starting on September 1, 1983 and ending on September 13, 1983 in an attempt to elucidate the effects of episodal events on river water quality.

METHODS

On September 1, 1983 a Phillips automatic water sampler was installed in the United States Geological Survey (USGS) Automatic Water Quality Monitor (AWQM) building located at Milltown on the United States side of the St. Croix River. This sampler was equipped with twenty-four 250 mL bottles and was programmed to fill a single bottle at twelve-hour intervals. The water was pumped from a submersed inlet permanently positioned in the St. Croix River at the site of the Milltown, N.B.-Milltown Hts., Me. International Bridge.

The first sample was collected at 1630 hours on September 1, 1983 with the final sample being taken at 0430 hours on September 13, 1983. The sampler was removed on September 13 and transported to the Water Quality Branch laboratory in Moncton, New Brunswick. Each sample was analysed for physical parameters and major ions using methods described in the NAQUADAT Dictionary (WQB, 1983).

Daily river discharge data for the sampling period were taken from

the USGS gauge located at Baring. In addition the USGS provided data from the AWQM situated at Milltown. The Georgia-Pacific Corporation supplied data on effluent discharge rate, BOD loading, water colour and total suspended solids loading for the month of September. A map of the study area is presented in Figure 1.

RESULTS

The Georgia-Pacific Kraft Pulp Mill interrupted operation on September 4, and remained inoperative until September 18. From the effluent discharge rates, BOD loads and total suspended solid loads (Table 1), it is obvious that both shut-down and the subsequent start-up are not instantaneous, but rather span a couple of days. For example, although the mill was operative by September 18, it was not until September 20 that the system was up to full production. In addition, although the mill was inoperative for fourteen days, effluent discharge never ceased completely. This results from the practice of gradually reducing the treated effluent flow rate out of the #2 aeration lagoon before mill shutdown to raise the surface elevation of mill effluent (hence the volume) in the two aeration lagoons. Experience has taught the waste-water treatment plant operators that raising the mill effluent level in the aeration lagoons before a planned mill shut-down will allow them to make a more controlled release of treated effluent from the waste-water treatment plant during this period (Pers. comm. with G. Pierce). The minimum effluent discharge rate and BOD loading occurred on September 7, approximately three days after the plant shut-down. From

September 8 to September 17, the effluent discharge, BOD loading and total suspended solids loads were respectively, 50%, 10% and 20% of the characteristic operational levels.

The major ion concentrations and physical parameter values for each sample are given in Table 2. The major ion concentrations began their response to the mill shut-down during September 7 and fell rapidly throughout the following day. From September 9 to September 11, the ion concentrations remained relatively stable, being intermediate to the pre-shutdown and the background station levels (Table 2). The major ions which showed the greatest response were sodium and chloride and to a lesser extent sulphate and total alkalinity (Figure 2). These ions are used extensively in the Kraft process and thus are found in high concentrations in the effluent discharge (Howell and Lockerbie, 1983). As would be expected, the specific conductance also shows a significant response to the mill shut-down (Figure 3). Calcium, magnesium and potassium are not extensively used in the Kraft process and thus do not reflect the reduction in effluent discharge. In fact, the values recorded for these ions are similar to those found at the background station.

Water colour also responded to the reduced effluent loading while other parameters such as turbidity and pH showed no significant changes throughout the period. The data for the AWQM (Table 3) at Milltown indicated a response in specific conductance but no significant changes in pH, water temperature or dissolved oxygen concentration.

DISCUSSION

Although production at the Georgia-Pacific Kraft Mill ceased on September 4, there was no significant reduction in effluent loading until September 7. This three-day lag is probably a consequence of the eleven-day retention time of the secondary treatment facility.

Scrutiny of the major ion data suggests that there is a rapid in-river response at Milltown to reduction of effluent loading at Woodland. However, in order to get a better indication of the relationship between effluent discharge and downstream major ion concentrations, a series of linear regressions were performed. As there were no measurements of effluent major ion concentrations, it was necessary to use BOD values as indicators of ion concentration.

The major ion chemistry at Milltown depends not only on the effluent load but also on the river discharge. During the sampling period, there was approximately a 50 percent reduction in river discharge which would tend to damp the effects of the reduced effluent loading. In order to account for the effects of changing river discharge, flow weighted BOD concentrations were calculated for use in the regression analysis. Figures 4 to 7 show the relationship between specific conductance at Milltown and the flow-weighted BOD concentrations at four lag intervals. It must be emphasized that these regressions are not intended for any predictive purpose, other than to

provide insight into the time lag between effluent loading at Woodland and ion chemistry response at Milltown. Figure 4 assumes an immediate response to effluent loading, and has several outlying values. These outliers correspond to periods of rapidly changing BOD loading, indicating that there is a lag in response. Addition of lag intervals by 12 hour increments, decreases both the number and extent of outliers, with the best relationship found for a 24-hour lag period (Figure 6). Similar results were observed for those major ions (Na, Cl, SO_4, Total Alkalinity) which are significantly affected by effluent loading. This would suggest that at a river discharge rate of approximately 1000 cfs (28.3 cms), there is a lag or travel time of approximately twenty-four hours, between Woodland and Milltown. This agrees well with a travel time of 15.5 hours at a river discharge rate of 1860 cfs (52.7 cms), estimated using fluorescent dye (MS. Report, 1971).

Although these relationships between BOD concentration and major ion concentrations appear to be useful to indicate response lags, they are of limited predictive use. In fact, any use of these relationships assumes that there is a relationship between effluent BOD and effluent major ion concentrations. This assumption may not be completely valid as without exclusion of data from September 1 and 2, when the mill was in full production, the previously presented linear relationships would be extremely poor. Effluent BOD concentrations depend not only on the concentration of dissolved organic compounds but also on the concentration of total suspended solids. These dissolved organic

compounds found in the black liquor are probably related to the effluent major ion concentrations, as both depend on the rate of mill production. However, it is unlikely that the effluent major ion concentrations are closely related to the total suspended solids. Thus it appears that BOD concentrations are related to major ion levels only during periods when total suspended solids in the effluent are relatively constant. Total suspended solid values for September 1 and September 2 (Table 1) were much higher than for other days during the sampling period which explains the necessity for their exclusion from the regression analysis.

The parameter of particular concern on the St. Croix River is the dissolved oxygen concentration or percent saturation. As dissolved oxygen concentration is related to BOD loading, it was expected that the mill shut-down would elicit an increase in Milltown dissolved oxygen. However, at the AWQM (Table 3) there was no significant change in either the concentration or saturation of dissolved oxygen over the study period. It is possible that this lack of apparent response is a consequence of reduced flow during the study period. This reduction in river discharge both increases the travel time and allows greater contact with the sediments. In the past, logging and wood processing activities in the St. Croix River Basin have resulted in the accumulation of wood fibre in the river sediments and a subsequent increase in sediment oxygen demand (MS. Report, 1971). Presently, it is probable that sediment oxygen demand is still an important determinate of overlying oxygen conditions, particularly during periods of low

water.

Maintenance of oxygenated conditions in the St. Croix River is important during the critical periods when the Atlantic salmon are present. Since 1978, the water quality objectives of 5.0 mg/L O_2 or 60% saturation have generally been met, although there have been occasional episodal events which have resulted in drastic oxygen reductions and subsequent fish kills. Thus, in order to ensure the continuation of an Atlantic salmon run in the St. Croix, it will be essential to avoid episodal oxygen depletions during critical periods.

In order to better understand the oxygen regime of the St. Croix River, a predictive oxygen model was developed by Boutot and Clair (1981). This model uses BOD loadings, water temperature and river discharge rate to estimate oxygen concentrations at numerous nodal points between Woodland and Milltown. Although this model makes accurate oxygen predictions, it is too complex to be used to make short term flow adjustments in order to avoid oxygen depletion. The 1982/1983 St. Croix River Water Quality Report (Howell and Lockerbie, 1983) indicated that there was a good inverse relationship between specific conductance and dissolved oxygen saturation. It was suggested that specific conductance was indirectly related to effluent BOD and thus may be a useful indicator of dissolved oxygen. This is particularly useful as the AWQM specific conductance probe is much more dependable than the AWQM oxygen sub-system and thus a relatively uninterrupted monitoring of specific conductance is possible.

However, data collected from 1978 to 1981, indicates that although low oxygen saturations were found during periods of high specific conductance, the linear relationship was poor ($r = -0.46$). It seemed that there was a greater dissolved oxygen response to effluent loading during the summer months, probably due to increased metabolic activity in warmer waters. Therefore in this presentation, water temperature was included into the linear regression analysis. The results of this regression analysis are presented in Table 4 and indicate that there is a good relationship between specific conductance, water temperature and percent saturation of dissolved oxygen, having a multiple correlation co-efficient of 0.80.

Using this multiple regression analysis, a nomogram was prepared (Figure 8) which predicts dissolved oxygen saturation from specific conductance and water temperature. Comparison of predicted Milltown oxygen saturation with actual AWQM values (Figure 9) indicates that the linear model generally predicts slightly lower values than observed. The lower predicted values are desirable as they will correct for possible prediction and sampling errors. Similar observations can be made using grab samples collected by both the Water Quality Branch and the United States Geological Survey (Figure 10).

However, the AWQM data indicates that below 65 percent saturation, some observed values are lower than predicted. There are numerous possible explanations for this poor predictability. The data for the

regression analysis was from a series of grab samples collected at Milltown between the years 1978 to 1981. The lower limit of oxygen saturation of these data was at or near to the 65 percent level and thus poor predictability below 65 percent saturation would be expected. Also, grab samples and AWQM data for both dissolved oxygen and specific conductance are not always in agreement, suggesting that there would be greater prediction error associated with using AWQM data.

Apart from these errors, the regression co-efficient indicates that variations in water temperature and specific conductance explain only 64 percent of the variation in dissolved oxygen saturation. Thus the multiple regression presently ignores some important variables. It may be that during low flow periods that the sediment oxygen demand becomes more important. However, incorporating river discharge into the regression as an indicator of low water periods proved to be statistically insignificant and resulted in no improvement in the predictive ability of the regression equation. Another possibility may be that occasional increased total suspended solids loads result in higher than expected river BOD concentrations. It may be possible in the future to incorporate variables such as suspended solids or stage height which may serve to improve the predictive capability of the multiple linear regression.

In spite of the insensitivity of the predictive equation at low oxygen saturation, the nomogram is still of use in an "early-warning" capacity. The present oxygen saturation objective for the St. Croix

River is 60 percent, below which values are considered to be of concern with respect to the survival of the Atlantic salmon. Although the nomograph appears to be applicable only to a saturation value of 65 percent this is probably adequate. As there is approximately a twenty-four hour travel time from Woodland to Baring, it is necessary to allow for a lag in response to increased river discharge. Thus once the predicted oxygen values range between 65-70 percent, remedial action may be warranted. Precautionary actions such as increasing the river discharge from the Grand Falls Dam above Woodland in order to increase oxygen saturations to "acceptable" levels may ensure the continuation of the Atlantic salmon run in the St. Croix River.

REFERENCES

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ACKNOWLEDGEMENTS

The author would like to thank Mr. G. Pierce of the Georgia-Pacific Corporation for providing data on effluent discharge during the study period. Appreciation is due to the United States Geological Service who provided discharge and Automatic Monitor data. I am thankful to the Analytical Services Division for water quality analysis and Mrs. L. Boulter for typing the manuscript. The review and criticism of the manuscript by Messrs. D. Cullen, T. Clair, R. Arseneault, D. Lockerbie and Dr. T. Pollock was greatly appreciated.

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Table 4 Multiple Regression Analysis of Dissolved Oxygen Percent Saturation against Specific Conductance and Water Temperature.

TABLE 1: River and effluent discharge rates, BOD and Total Suspended Solids loads and Flow-weighted BOD concentrations for the St. Croix River from September 1 to 20, 1983

DATE	River Discharge cms	Effluent Discharge MG/day	Suspended Solids lbs/day	BOD lbs/day	Flow-weighted BOD mg/L
Sept. 1	60.1	24.8	15294	5270	0.460
2	55.2	21.5	11839	3902	0.370
3	56.3	10.0	6843	1940	0.181
4	60.6	10.0	5675	1878	0.163
5	45.9	10.0	4840	1690	0.193
6	31.4	8.2	3969	1232	0.206
7	28.9	2.7	1307	304	0.055
8	29.4	9.2	3548	478	0.085
9	27.4	9.7	1136	406	0.078
10	27.4	10.4	2265	540	0.103
11	27.5	11.2	4118	468	0.089
12	28.6	12.2	3448	588	0.108
13	29.7	11.7	1952	1464	0.259
14	29.5	12.2	2028	1825	0.325
15	29.2	12.5	4186	2325	0.419
16	29.2	11.7	2148	390	0.070
17	38.8	17.5	4970	526	0.071
18	51.0	18.4	5841	1168	0.121
19	49.9	19.4	7767	647	0.068
20	48.7	23.9	10257	7873	0.851

TABLE 2: Concentrations of major ions in twenty-four Milltown Automatic Sampler samples and two Kellyland background samples

DATE	Ca	Mg	K	Na	Cl	SO_4	Tot. Alk.	Spec. Cond.
				mg/L				uS/cm
Sept 1	3.6	0.6	0.7	9.8	7.9	7.7	10.8	75
2	3.8	0.6	0.8	10.0	9.2	7.8	11.0	76
2	3.9	0.6	0.8	10.5	9.1	7.6	12.0	80
3	3.8	0.6	0.8	9.7	9.1	6.5	11.7	75
3	3.7	0.6	0.8	8.5	6.7	6.6	10.7	68
4	3.8	0.6	0.8	10.0	8.6	7.3	11.8	77
4	4.0	0.6	0.8	11.7	10.3	8.0	13.2	86
5	4.0	0.6	0.8	11.3	9.7	7.9	12.1	84
5	3.9	0.6	0.8	10.1	9.0	7.2	11.9	77
6	4.1	0.6	0.9	12.4	10.6	8.8	13.0	91
6	4.0	0.7	0.9	11.5	10.0	8.1	13.2	87
7	4.0	0.7	0.8	11.7	9.3	8.2	12.8	85
7	3.7	0.6	0.8	9.0	7.4	7.2	12.2	72
8	3.5	0.6	0.7	6.6	5.3	5.9	10.2	57
8	3.4	0.6	0.5	5.6	4.6	5.4	9.4	51
9	3.4	0.6	0.5	5.0	4.4	5.4	9.2	48
9	3.4	0.6	0.5	4.9	4.2	5.2	9.0	49
10	3.4	0.6	0.7	4.8	4.4	5.4	8.8	49
10	3.4	0.6	0.4	5.1	4.7	5.5	9.2	51
11	3.4	0.6	0.5	5.2	4.4	5.7	9.5	50
11	3.4	0.6	0.9	5.5	4.9	6.3	9.3	52
12	3.4	0.6	0.4	5.6	5.1	5.4	9.6	52
12	3.6	0.6	0.5	5.9	5.2	5.5	9.5	56
13	3.6	0.6	0.7	5.9	5.2	5.7	10.0	56
Kellyland								
Sept 1	2.9	0.5	0.4	1.5	1.4	3.0	6.0	28
12	3.2	0.6	0.5	1.3	1.5	3.1	7.0	29

TABLE 3: Automatic Water Quality Monitor data for the St. Croix River on a twelve hour frequency from September 1 to 13, 1983

DATE	Water Temperature °C	Spec Cond uS/cm	pH	Diss. Oxygen mg/L
Sept 1	20.5	90	6.7	6.4
1	21.3	88	6.8	6.6
2	20.9	81	6.7	6.7
2	21.4	87	6.8	6.8
3	21.6	78	6.8	6.9
3	21.5	72	6.7	6.9
4	22.5	84	6.7	6.8
4	22.4	94	6.8	6.8
5	21.9	88	6.8	6.7
5	22.5	81	6.7	6.6
6	23.3	97	6.8	6.6
6	23.0	91	6.7	6.1
7	23.5	90	6.8	6.5
7	23.5	75	6.7	6.1
8	22.5	60	6.7	6.6
8	22.0	56	6.7	6.6
9	20.7	52	6.7	7.2
9	21.0	53	6.7	6.7
10	20.9	52	6.7	7.1
10	21.9	54	6.7	6.5
11	21.9	54	6.7	6.7
11	21.9	56	6.7	6.7
12	21.4	57	6.7	6.8
12	21.8	59	6.7	6.9
13	21.4	59	6.7	7.2
13	21.7	60	6.7	7.0

TABLE 4: Multiple Regression Analysis of Dissolved Oxygen Percent Saturation against Specific Conductance and Water Temperature

D.O. (Sat'n) = -0.1049 Sp. Cond. - 0.789 Temp + 98.3 F = 39.4**

F = 8.8* 52.7** 1308**

Multiple r = 0.80 r^2 = 0.64 n = 48

* p=L .005 ** p=L .001

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Figure 7 Relationship between flow-weighted BOD concentration and specific conductance, assuming a 36 hour response lag.

Figure 8 Nomograph to predict percent oxygen saturation from specific conductance and water temperature.

Figure 9 Relationship between predicted and observed oxygen saturation values for Milltown AWQM data.

Figure 10 Relationship between predicted and observed oxygen saturation values for Milltown grab sample data.

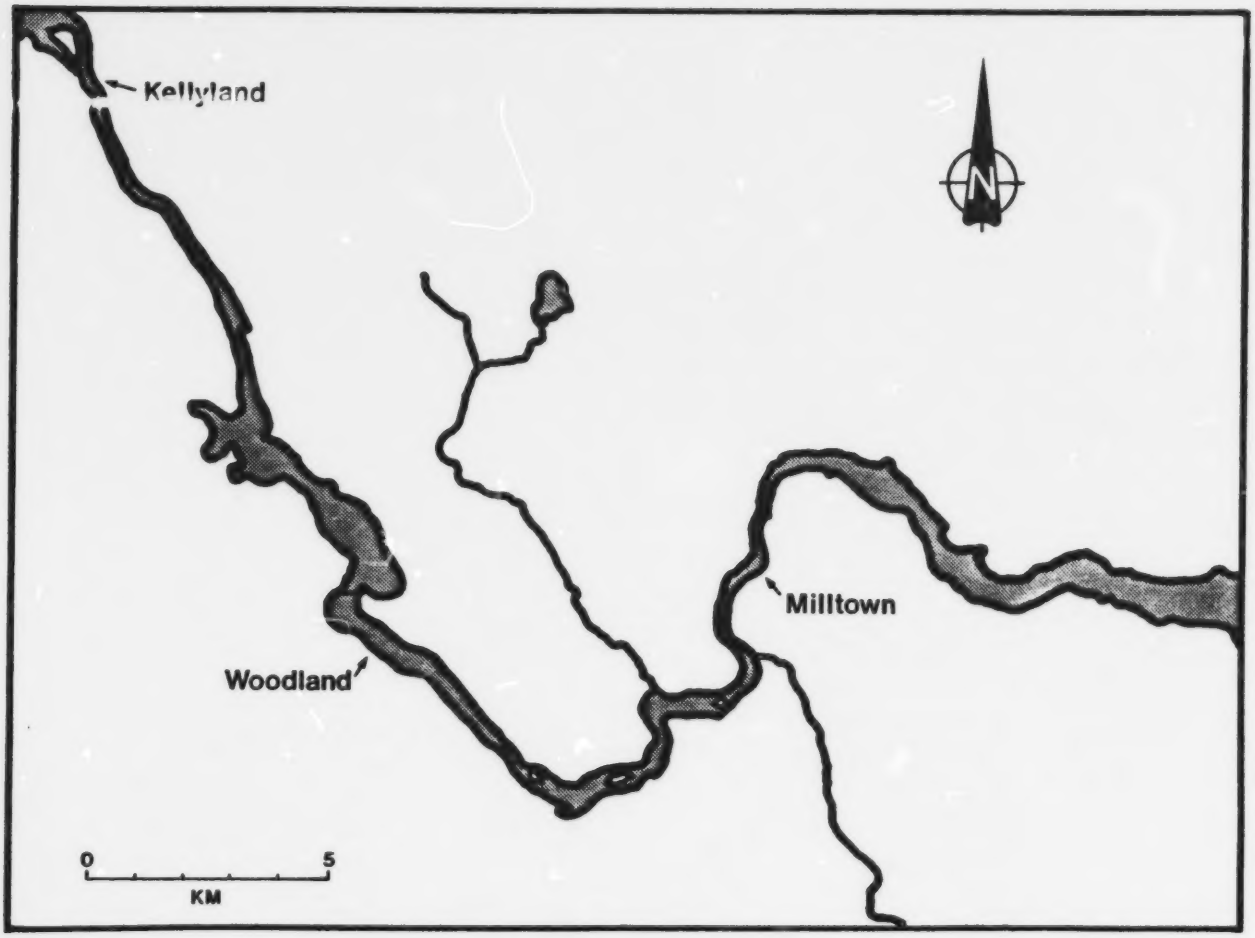

FIGURE 1 THE STUDY AREA

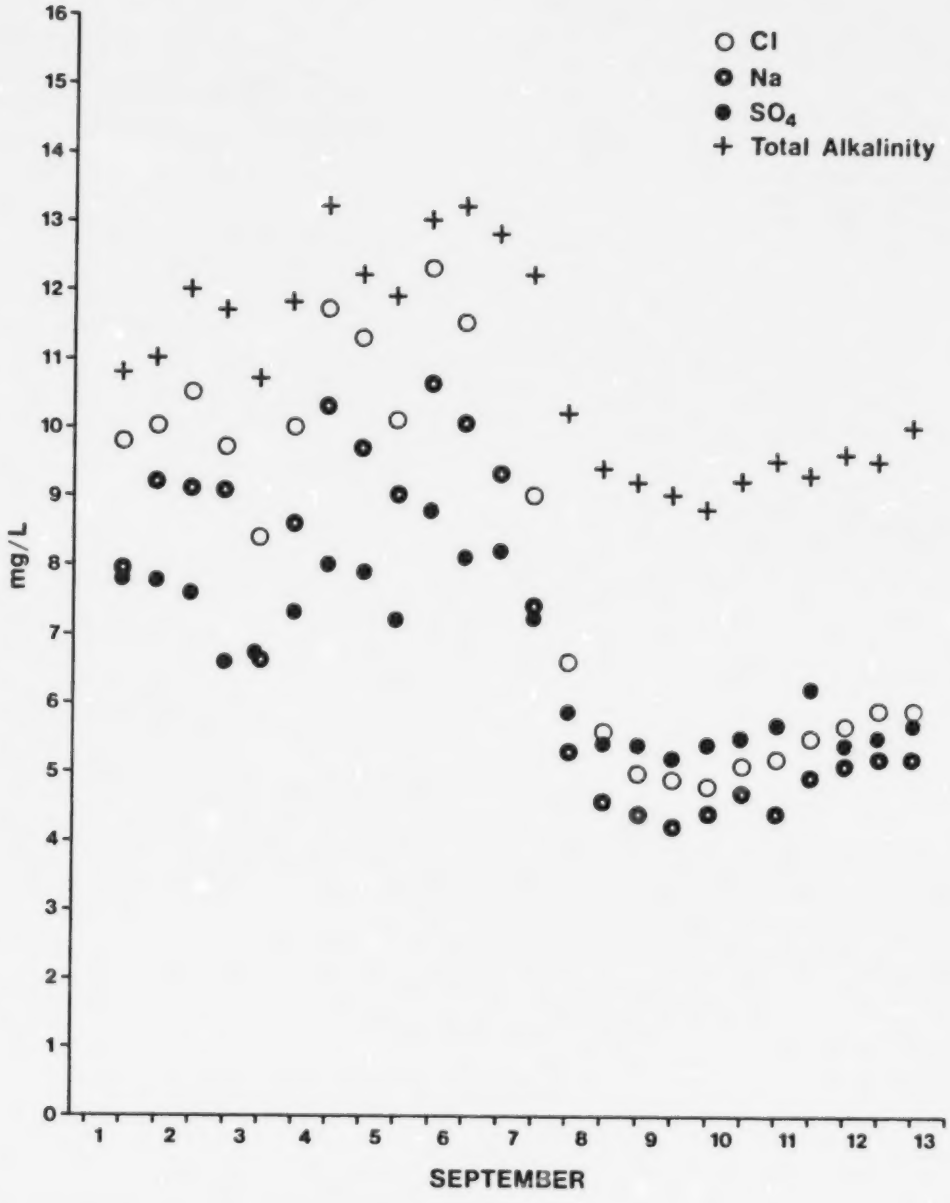

FIGURE 2 VARIATION IN SELECTED MAJOR ION CONCENTRATIONS OVER A 13 DAY PERIOD

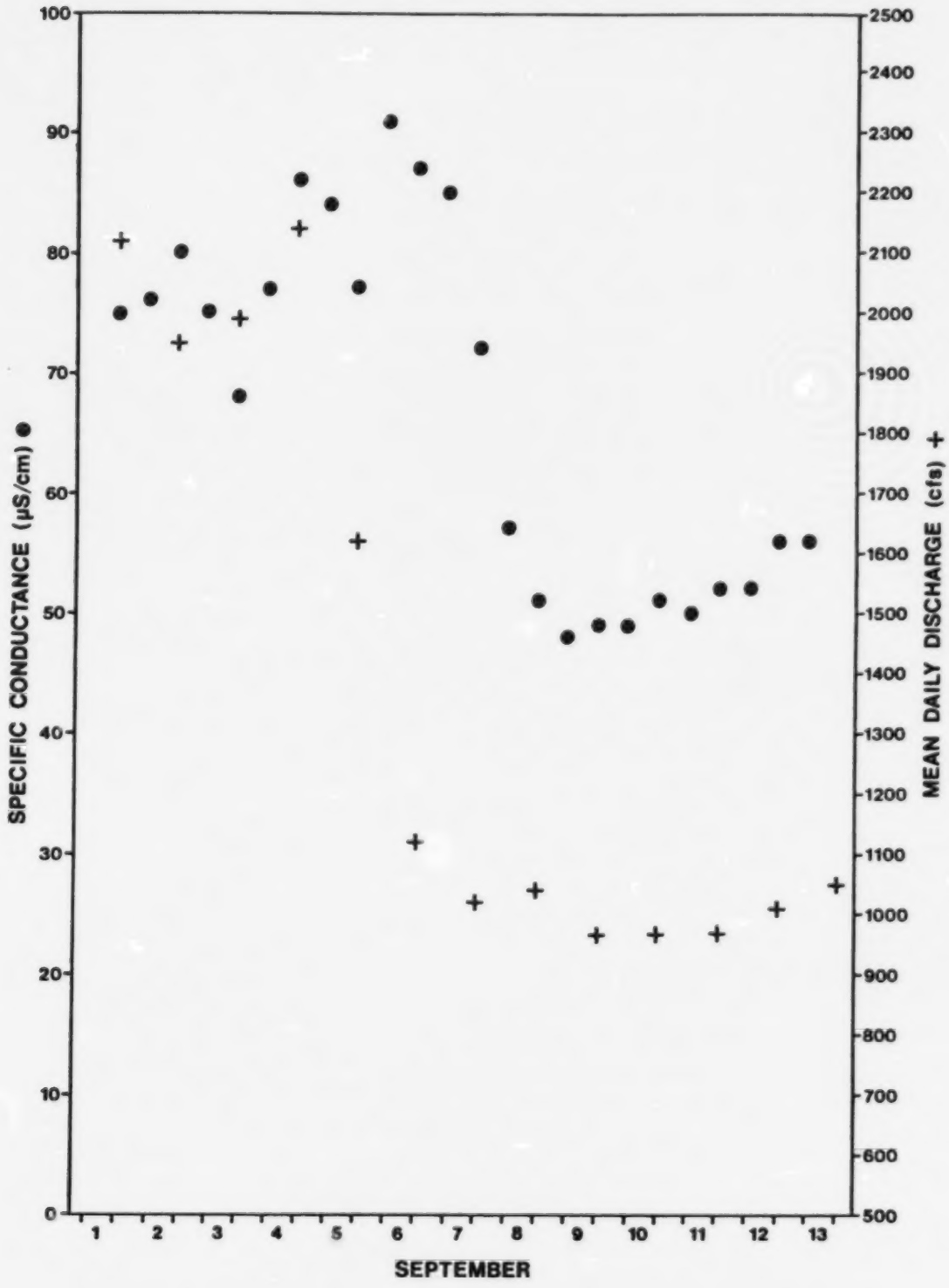

FIGURE 3 VARIATION IN SPECIFIC CONDUCTANCE AND MEAN DAILY DISCHARGE OVER A 13 DAY PERIOD

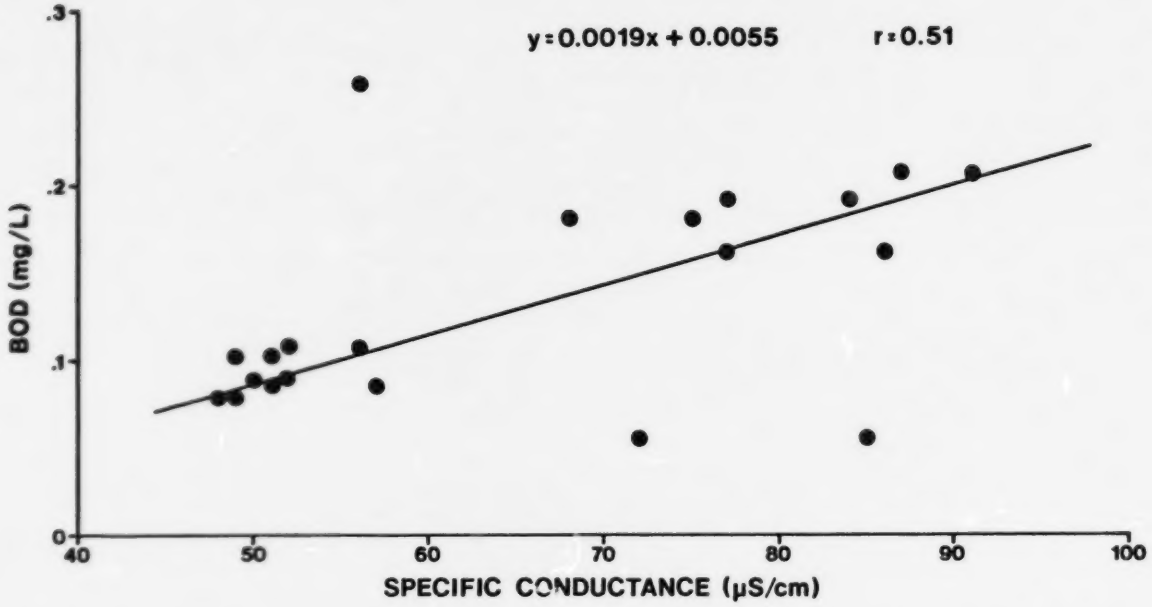

FIGURE 4 RELATIONSHIP BETWEEN FLOW-WEIGHTED BOD CONCENTRATION AND SPECIFIC CONDUCTANCE ASSUMING NO LAG IN RESPONSE TIME

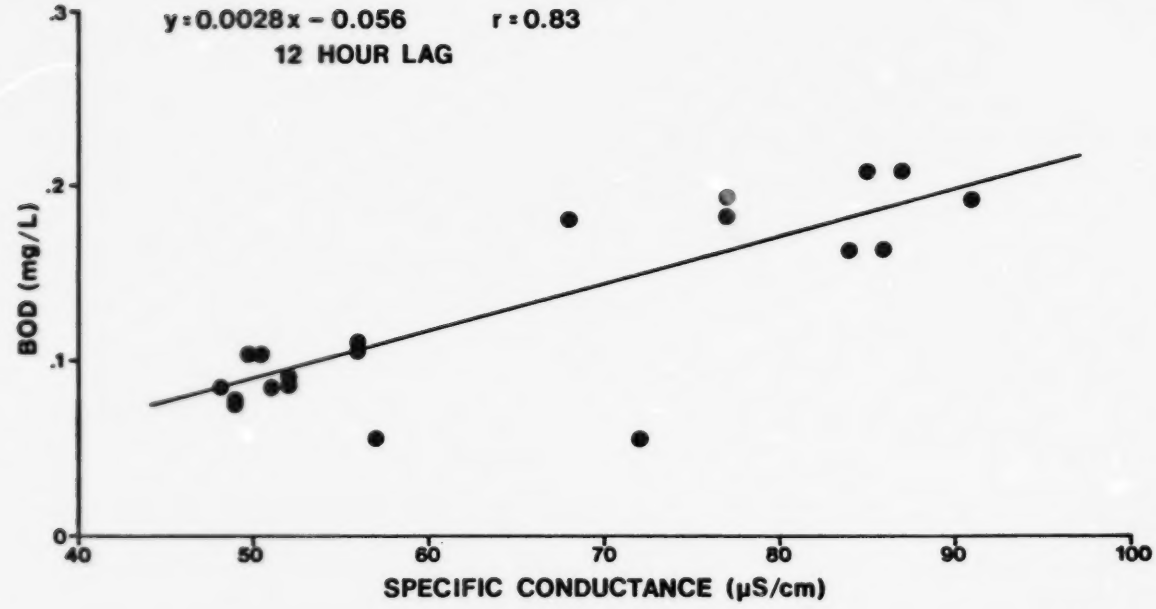

FIGURE 5 RELATIONSHIP BETWEEN FLOW-WEIGHTED BOD CONCENTRATION AND SPECIFIC CONDUCTANCE ASSUMING A 12 HOUR RESPONSE LAG

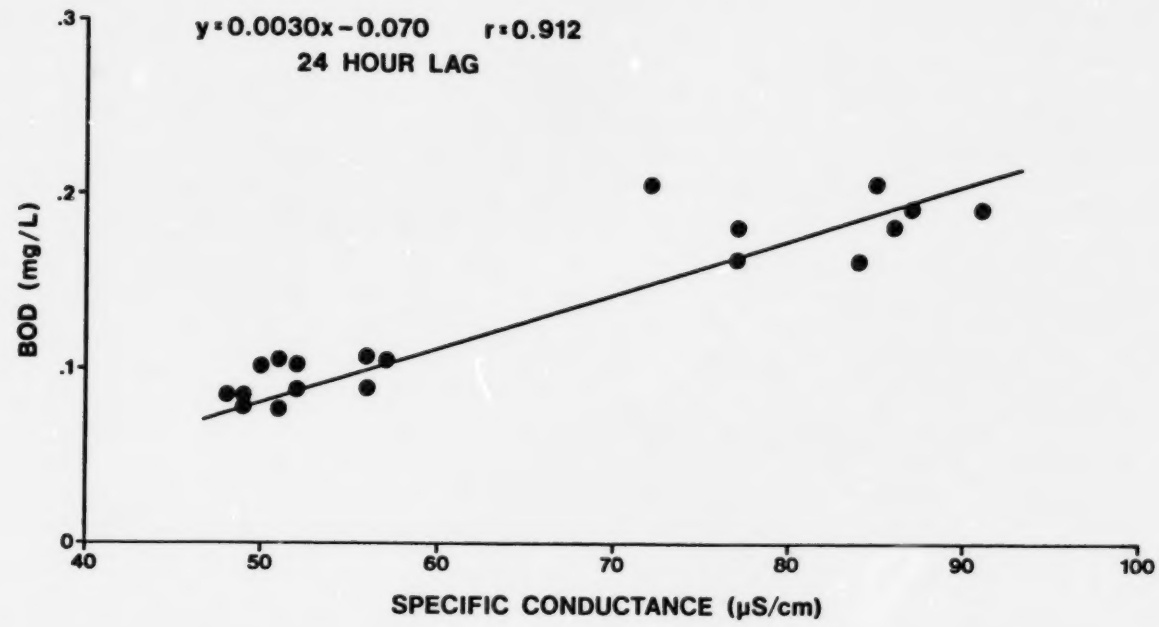

FIGURE 6 RELATIONSHIP BETWEEN FLOW-WEIGHTED BOD CONCENTRATION AND SPECIFIC CONDUCTANCE ASSUMING A 24 HOUR RESPONSE LAG

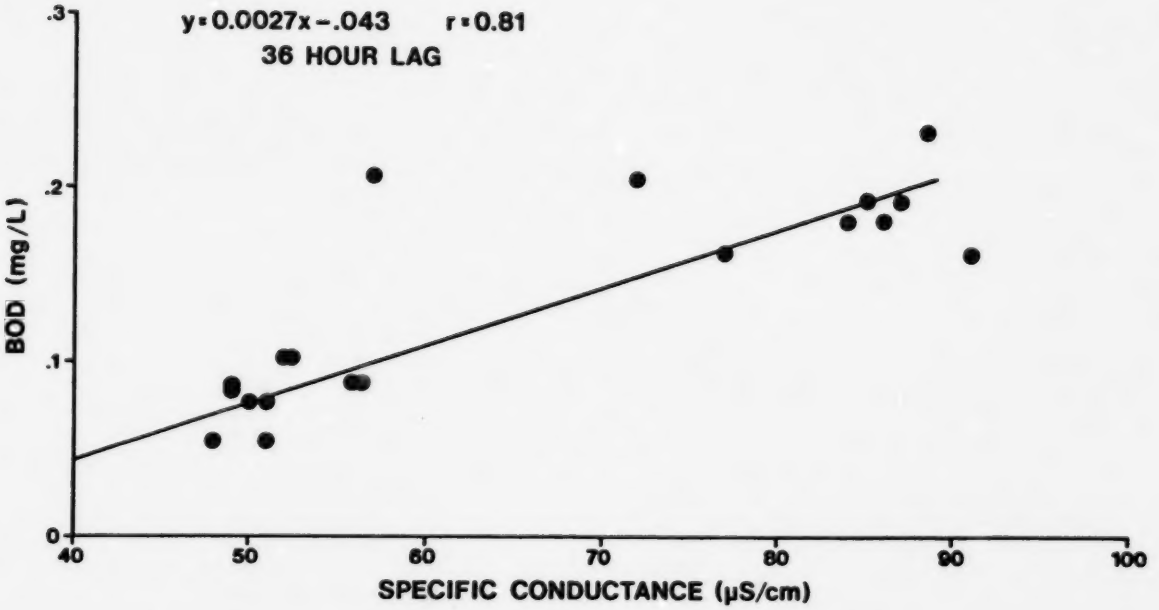

FIGURE 7 RELATIONSHIP BETWEEN FLOW-WEIGHTED BOD CONCENTRATION AND SPECIFIC CONDUCTANCE ASSUMING A 36 HOUR RESPONSE LAG

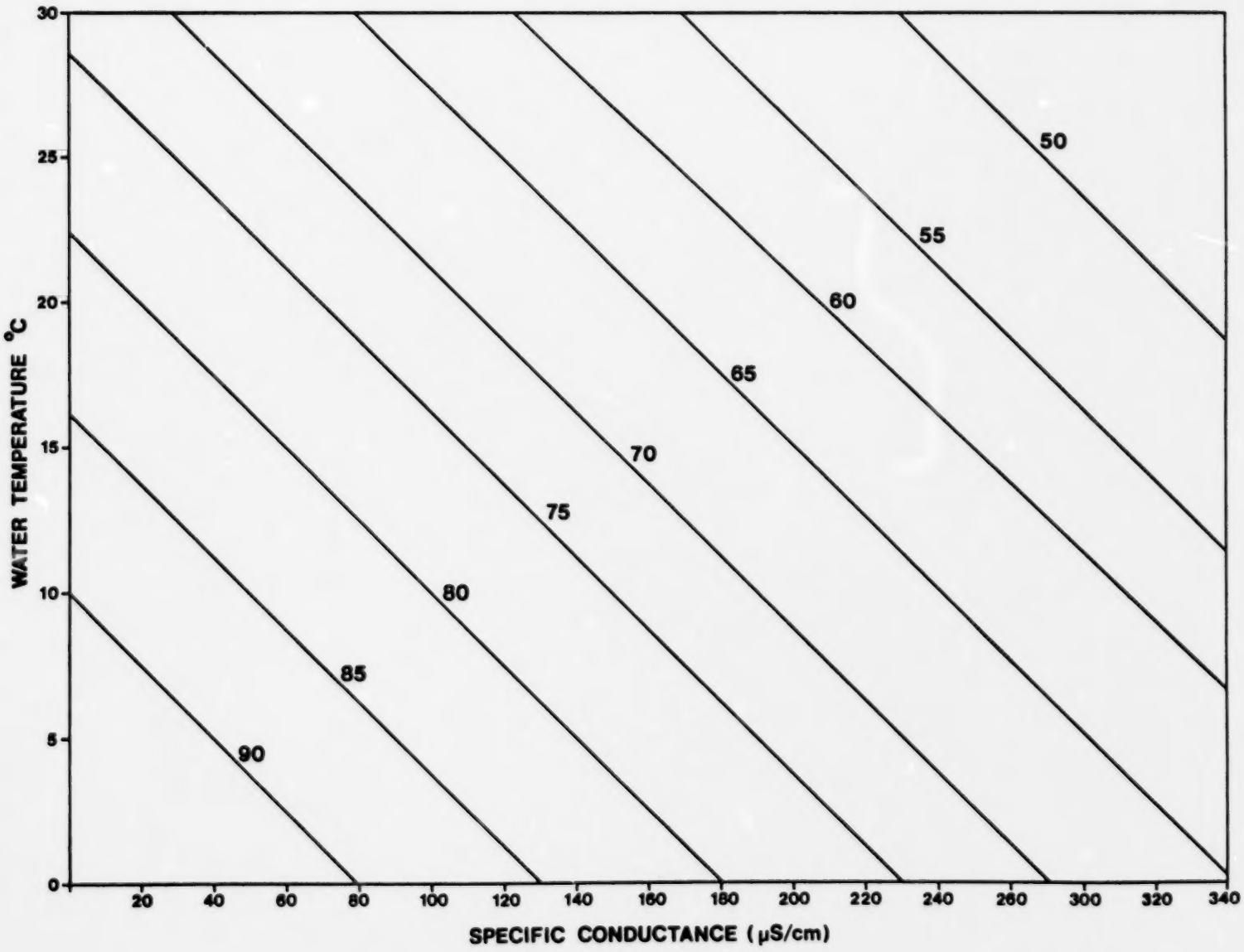

FIGURE 8 A NOMOGRAPH WHICH PREDICTS DISSOLVED OXYGEN SATURATION FROM SPECIFIC CONDUCTANCE AND WATER TEMPERATURE

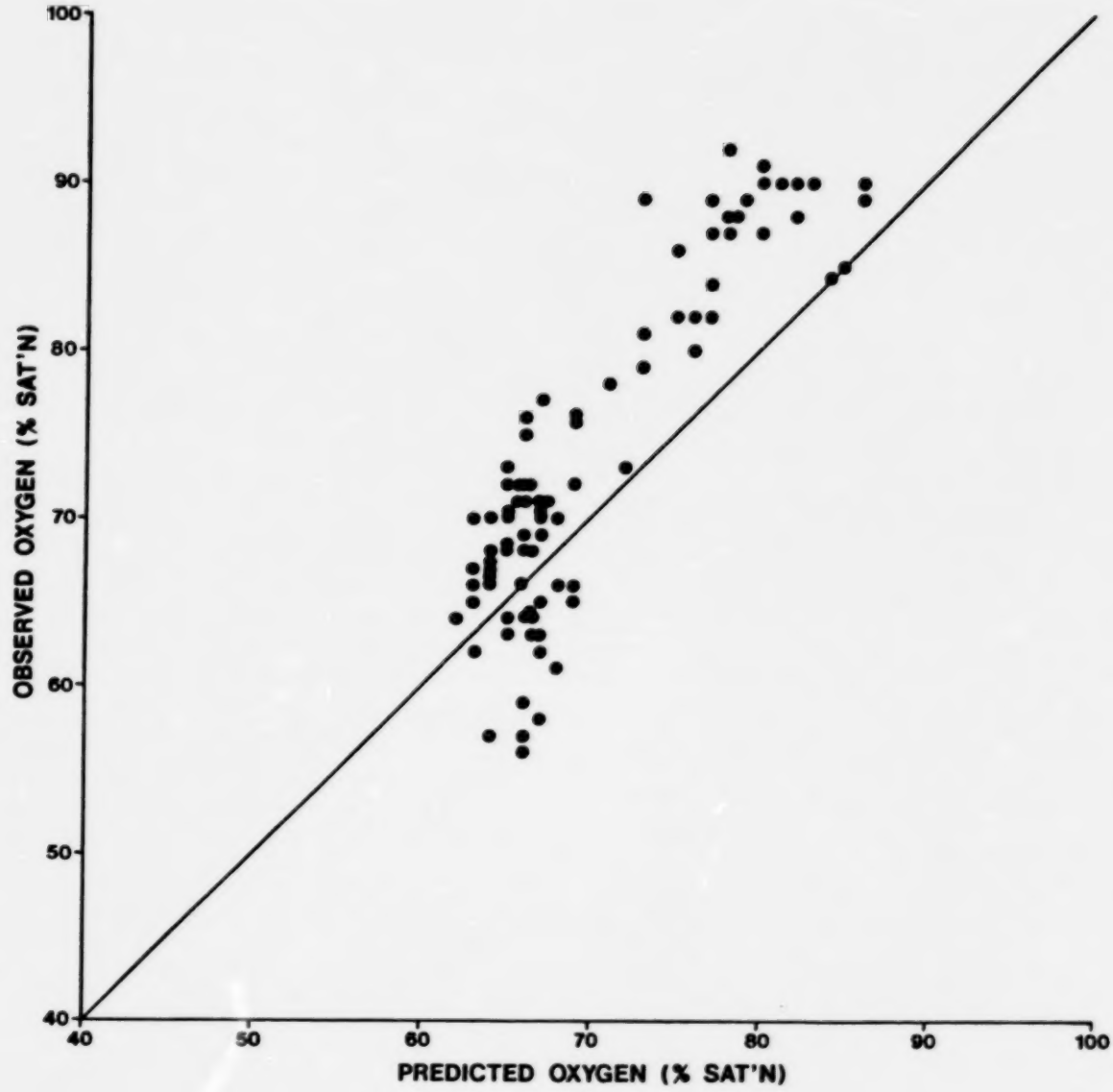

FIGURE 9 OBSERVED AND PREDICTED OXYGEN SATURATIONS USING THE ST. CROIX RIVER AWQM DATA

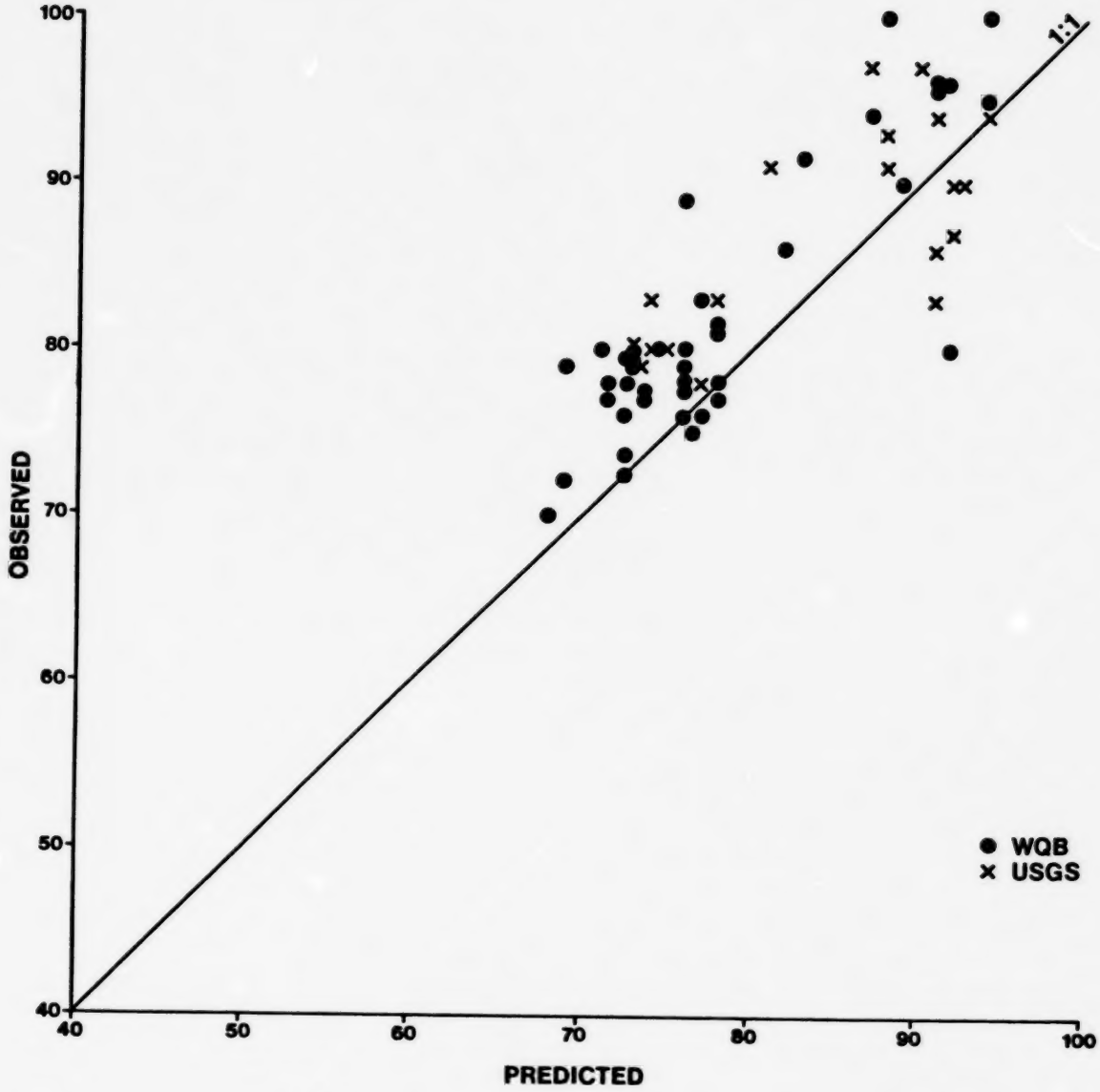

FIGURE 10 OBSERVED AND PREDICTED OXYGEN SATURATIONS USING WQB AND USGS GRAB SAMPLE DATA